

Why does PdTe have such a weaker superconductivity compared to FeSe? A First-Principle Wannier function analysis of the electronic structure of PdTe

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We report a first-principles Wannier function study of the electronic structure of PdTe in an attempt to understand why its superconducting T_c is much lower than, e.g., FeSe. We find that electronic correlation effects are reduced in PdTe due to its broad three-dimensional structure. In addition, the higher filling of the Pd d -shell, its stronger covalency resulting from the closer energy of the Pd- d and Te- p shells, and the larger crystal field effects on the Pd ion due to its near octahedral coordination all serve to weaken significantly electronic correlations in the particle-hole (spin, charge, and orbital) channel. This case study highlights the essential features (quasi-two-dimensionality, proximity to half-filling, weaker covalency, and higher orbital degeneracy) of Fe-based high-temperature superconductors.

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I. INTRODUCTION

The discovery of high-temperature superconductivity in the Fe chalcogenides^{1,2} led to a “gold rush” to find superconductivity in other non-cuprate materials. Compared with Fe-based superconductors,^{3–11} these non-toxic layered compounds with weak inter-layer van der Waals forces exhibit interesting physical properties, including phase separation,¹² strong correlations,^{13,14} non-trivial isovalent doping,^{15–17} Fe excess effects,¹⁸ Fe vacancy,^{19–21} and rich high-pressure phase diagrams.^{13,14,22–24} Attention has also shifted to other non-Fe transition metal based chalcogenides as they are shedding light on the road to the *post-iron age* in superconductivity.

Decades of study of the properties of Palladium monotelluride (PdTe) show that it has a $T_c \approx 2.3 - 4.5$ K,^{25–28} and a phase diagram reminiscent of the high-pressure diagram of Fe chalcogenides (FeCh).^{23,29} Compared with FeCh^{1,2,15,24,30} the hexagonal PdTe structure (c.f. Fig. I(a)) can be regarded as the deformed structure of FeTe (c.f. Fig. I(c)) obtained by sliding the anion and cation layers. Despite such structural similarity, the local ligand field is transformed from a tetrahedral cage surrounding Fe to an octahedral cage surrounding Pd. With a similar crystal structure but distinct physical properties, PdTe thus serves as a good candidate for comparison to better illuminate the important physical effects and to reveal the building blocks for a stronger superconductivity in the Fe chalcogenides.

Motivated by the evolving effort to understand the superconductivity mechanism in Fe-based superconductors, we provide a first-principles Wannier function analysis of the electronic structure of PdTe. By comparing the characteristics of PdTe with those of Fe chalcogenides,

one expects to identify key ingredients behind the high-temperature superconductivity in Fe-based superconductors, a current research topic of general interest to a broad audience. Our study illuminates the important underlying physics of the high- T_c Fe-based superconductors and most especially, reveals the building blocks for a stronger superconductivity in Fe chalcogenides. Such a study can help to reaccess the rules one uses in the search of a room temperature superconductor and in particular, providing key insights on how to achieve high temperature superconductivity in general. We find that the face-shared octahedral coordination of Pd and the larger size of its $4d$ orbital favor the electronic kinetic energy over the Coulomb potential energy. Also, in contrast to the FeCh, a broad three-dimensional Fermi surface (FS) with a strong variation along the k_z direction, and a lack of orbital degeneracy are observed. The almost fully occupied Pd d orbitals lead to a strong covalent Pd-Te bonding and a vanishing local magnetic moment. A near octahedral coordination in PdTe leads to a large crystal field splitting of the Pd- d orbitals ($t_{2g} - e_g$) with a crystal field parameter of $\Delta_{oct} \sim 400$ meV. Therefore, most probably electronic correlations are suppressed in pure PdTe.

II. APPROACH AND CRYSTAL STRUCTURE

We use first-principles calculations to study the electronic structure of PdTe and the competition between various magnetic configurations. We utilize standard density functional theory (DFT) within the general potential linearized augmented planewave (LAPW) method³¹ and the generalized gradient approximation (PBE-GGA) functional,³² as implemented in WiEN2k.³³ In our computations, we utilize the room temperature

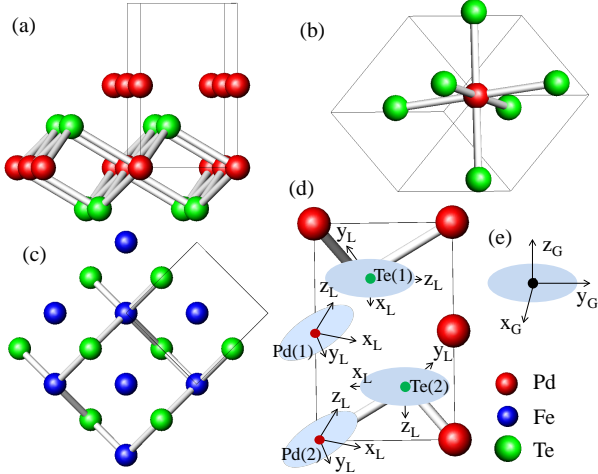


FIG. 1: (Color online) (a) The hexagonal structure of PdTe along the [001] direction. The positions of the atoms are Pd(1): (0,0,1/2), Pd(2): (0,0,0), Te(1): (1/3,2/3,3/4), and Te(2): (2/3,1/3,1/4), respectively. (b) The Pd-centered edge and face sharing environment with the neighboring octahedra. There are six Te octahedrally arranged around Pd. (c) The tetragonal structure of FeTe along the [001] direction. (d) The local coordinate of Pd and Te in the PdTe system as utilized in the definition of the Wannier basis. The local coordinates corresponding to each of the atoms in the unit cell (two Pd and two Te) have been defined using the x-convention. (e) The global coordinate of the PdTe system. The subscripts L and G denote local and global coordinates, respectively.

experimental lattice parameters: $a = b = 4.152 \text{ \AA}$ and $c = 5.672 \text{ \AA}$,³⁴ and the hexagonal crystal structure with space group $P6_3/mmc$ (Patterson symbol).³⁵ Pd and Te atoms occupy $2a$ and $2c$ Wyckoff positions, respectively, namely, Pd(1): (0,0,1/2), Pd(2): (0,0,0); Te(1): (1/3,2/3,3/4), and Te(2): (2/3,1/3,1/4).^{28,35,36} Thus, the first-principles ground state can be reached with all the WiEN2k default settings and a k -mesh of $14 \times 14 \times 9$. To downfold the DFT electronic band structure, symmetry respecting Wannier functions^{37–39} of Pd d and Te p are constructed to capture the low-energy Hilbert space within $[-8, 3] \text{ eV}$ and obtain an effective tight-binding Hamiltonian. We then obtain the band structure and the Fermi surface by calculating the orbital-resolved spectral function, $A_{n,k}(\omega)$, where n, k, ω are orbital index, crystal momentum, and energy, respectively.

The structure of PdTe is tied strongly to its electronic and magnetic properties, since the spatial extension of the $4d$ orbitals promotes comparable and competing kinetic and Coulomb energies. PdTe crystallizes in the NiAs crystal structure, which is of interest both from experimental and theoretical points of view.^{40,41} Transition metal compounds with the NiAs crystal structure attract special interest due to anomalies in their magnetic and electrical properties especially near phase transitions, the nature of which is still under study.⁴¹ In PdTe the Pd atoms sit in an fcc-like environment, while the Te atoms

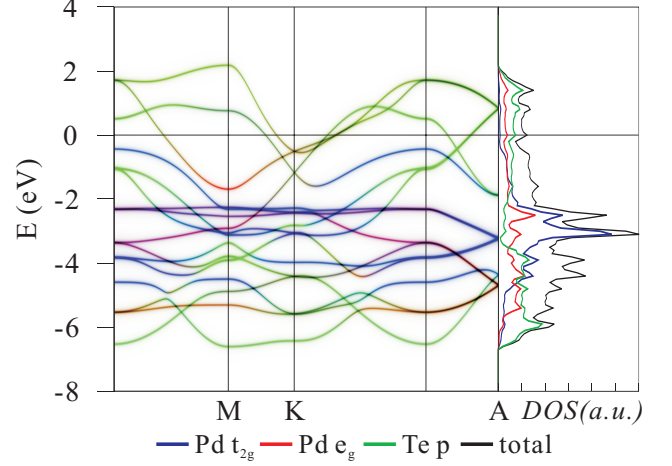


FIG. 2: (Color online) Left panel: Calculated dispersion (band structure) of PdTe within $[-8.0, 3.0] \text{ eV}$. Right panel: The corresponding spectra (in a.u. unit) as obtained from the symmetry respecting Wannier functions within $[-8.0, 3.0] \text{ eV}$. In both plots, the Fermi level is set equal to zero.

form an hcp-like structure and are surrounded by six Pd metal atoms forming a trigonal prism.⁴² In this structure, the Pd-centered octahedron shares both edges and faces with the neighboring PdTe_6 octahedra (c.f. Fig. 1 (a) and (b)). This is different from FeCh or FePn where the corrugated square planes of Fe with Se (or As) atoms are such that Fe is tetrahedrally coordinated below and above the planes. Thus, the Fe atoms sit in the tetrahedral cavities of the tetragonally distorted close packed lattice of Se (or As).⁴³ We also note that the structure of PdTe places Pd atoms closer to each other than in a perovskite; as such, direct Pd-Pd hybridization becomes important as we will discuss below.

III. RESULTS AND DISCUSSION

Our resulting electronic band structure and density of states (DOS) for non-magnetic PdTe are shown in Fig. 2, colored to emphasize the Pd t_{2g} , e_g and Te p orbitals. The whole spectrum is predominantly a single huge band due to the strong hybridization between Pd d and Te p orbitals. Notice from the DOS (c.f. Fig. 2) that almost all the Pd d orbitals are occupied, and the low energy excitations near the Fermi surface are composed mainly of Te p electrons hybridized with the e_g orbital of Pd. The Pd d orbital occupancy can be calculated from the trace of the one-particle reduced density matrix on each Pd atom (in Wannier function basis) and is found to be 9.31, which is very close to the fully occupied value of 10. This indicates strong covalency of the Pd-Te bonding and strong suppression of the spin local moment.

In Fig. 3, the Fermi surface is presented in different k_z planes. As already seen in the band structure, the states

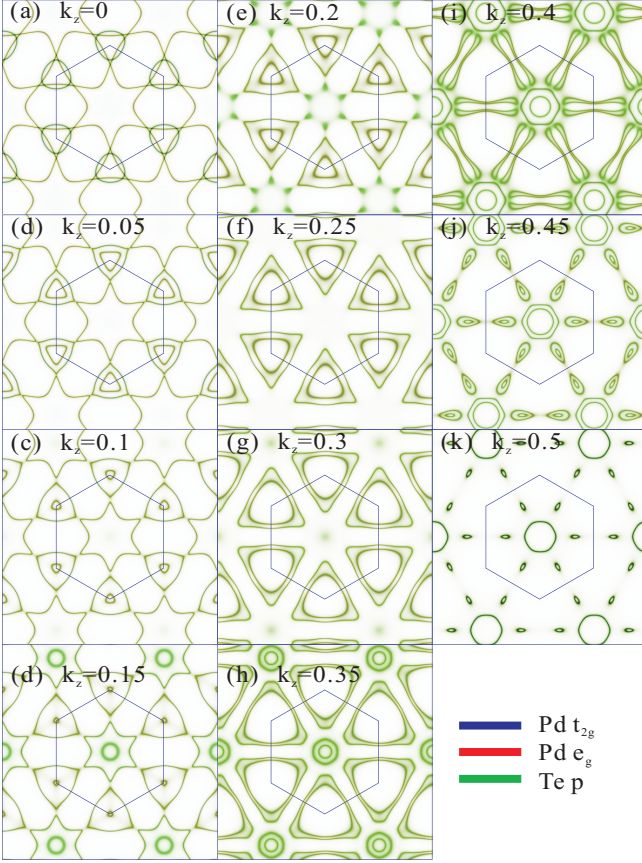


FIG. 3: (Color online) The Fermi surface of PdTe at different k_z planes with the same color code as Fig. 2. The value of k_z is in units of $2\pi/c$. The states in the proximity of the Fermi surface are predominantly Te- p states, hence the color of the Fermi surface plots is mainly green.

in the proximity of the Fermi level consist mainly of Te p (green orbital) weakly hybridized with Pd e_g (red orbital), thus appearing dark green. The Fermi energy is located close to the local minimum of the DOS, corresponding to $N(E_F) \approx 2.41$ a.u. The strong k_z variation of the Fermi surface topology also demonstrates a strong three dimensional character of the electronic structure.

To investigate the magnetism of PdTe, we survey various magnetic configurations, including collinear, bi-collinear, and checkerboard antiferromagnetism, with spin-polarized calculations. Indeed, the non-polarized case possesses the lowest ground state total energy, so there are no long-range magnetic correlations. This is consistent with the fact that the almost-full-Pd- d orbitals not only rule out the superexchange mechanism for antiferromagnetic correlations, but also suppress the effectiveness of Hund's coupling, and thus ferromagnetic correlations as well.

In order to gain a microscopic insight into the electronic structure of PdTe, we transform the self-consistent Kohn-Sham (DFT) Hamiltonian to Wannier basis, as

summarized in Table I. In the intra-atomic Pd block, one finds a large (~ 400 meV) $t_{2g}-e_g$ splitting which originated from the octahedral ligand field, with negligible off-diagonal terms associated with the tiny distortion of the octahedral cage. A similar splitting (~ 500 meV) is also found between Te p_z and p_x/p_y . Furthermore, we find considerable inter-atomic Pd-Te and Pd-Pd hopping, for example, $t_{Pd(1)_{z^2}, Te(1)_{p_x}} = 509$, $t_{Pd(1)_{z^2}, Te(1)_{p_y}} = 881$, $t_{Pd(1)_{x^2-y^2}, Te(2)_{p_x}} = -881$, $t_{Pd(1)_{z^2}, Te(1)_{p_z}} = 559$, and $t_{Pd(1)_{xy}, Pd(2)_{d_{xy}}} = -353$ meV, which are much larger than the intrinsic scale for the on-site energy difference between Pd and Te (~ 100 meV) (c.f. Table I). The same hopping value of $t_{Pd(1)_{z^2}, Te(1)_{p_y}}$ and $t_{Pd(1)_{x^2-y^2}, Te(2)_{p_x}}$, even when they are not symmetry related, is due to the 30° tilting angle that is naturally built-in in the crystal symmetry of PdTe, as can be understood from the Slater-Koster coefficients used in the tight-binding model.^{44,45}

TABLE I: (Color online). This table is mainly intended to show the hopping dominated physics in PdTe and, as such, it represents a reduced matrix of the original 16 by 16 matrix of Pd d and Te p states. For clarity, the Pd(1) d and Te(1) p sub-bands are represented using bold letters. The expectation value $\langle WF_i | H | WF_j \rangle$, where WF_i corresponds to the Wannier function of orbital i , is denoted as $\langle n | H | n' \rangle$ on the table. On-site energies of Pd d orbitals, split due to crystal fields into e_g (z^2 and $x^2 - y^2$) (red) and t_{2g} (yz , xz , and xy) (blue) sub-bands, and the Te p_x , p_y , and p_z sub-bands (green), and the hopping integrals among Pd d and Te p Wannier orbitals for the nonmagnetic case are displayed. Units are meV. The local coordinates of each of the atoms are defined in Fig. I(d).

$\langle n H n' \rangle$	z^2	$x^2 - y^2$	yz	xz	xy	x	y	z
z^2	-2608	0	2	2	4	509	881	559
$x^2 - y^2$	0	-2608	-4	4	0	38	-22	0
yz	2	-4	-2987	-42	42	187	-290	361
xz	2	4	-42	-2987	42	-345	17	361
xy	4	0	42	42	-2987	26	45	33
x	509	38	187	-345	26	-3112	0	0
y	881	-22	-290	17	45	0	-3112	0
z	559	0	361	361	33	0	0	-2597
z^2	-20	0	60	60	120	8	14	50
$x^2 - y^2$	0	20	104	-104	0	-22	13	0
yz	60	104	-150	-353	150	2	0	-33
xz	60	-104	-353	-150	150	-1	1	-33
xy	120	0	150	150	-353	18	31	-1
x	509	-881	52	158	-158	79	254	263
y	-38	-22	0	307	307	254	-214	-455
z	279	-484	33	-361	361	-263	455	524

Unconventional superconductivity generally emerges in frustrated systems⁴⁶⁻⁵⁰ when long-range order in the spin, charge or orbital channel is suppressed. The key ingredients needed for a typical unconventional superconductor, strong short-range correlations in these channels, are either negligible or dilute in PdTe.

Several factors make PdTe very different from FeCh. Strong hopping due to the more extended $4d$ orbitals, which promotes a larger kinetic energy, closer Pd-Pd distance in the face-shared Pd octahedron environment, negligible Hund's moment, weaker magnetic spin fluctuations, lack of orbital degeneracy, strong covalency, and very dilute magnetic frustration. Although PdTe has a layered structure similar to the tetragonal Fe chalcogenides, its intrinsic Pd $4d$ character and face-shared octahedron environment not only suppress the electronic correlations in the charge, orbital, and spin channels but also promote three dimensionality. The three dimensionality of PdTe electronic structure is made clear from the strong k_z dependence of the Fermi surfaces in Fig. 3. Such a strong three-dimensionality indicates a much weaker Fermi surface nesting, and would likely favor a weaker long-range correlation in the particle-hole (spin, charge, and orbital) channel. In addition, since the charge-transfer energy between Pd d and chalcogen p states is much smaller in PdTe than in FeCh, the Pd d states are almost fully occupied, and there are no states available to form a large Hund's moment, making magnetic correlations and, e.g., magnetic frustration effects, weaker. Therefore, the relatively lower superconducting temperature of PdTe, in comparison to most Fe superconductors^{1,2,14,17,51-53}, is not surprising.

As can be seen from Table I, the dominant hoppings are those between Pd and the neighboring Te. This strong hopping is due to the large orbital overlap between Te and Pd ions (c.f. Fig. I(d)). On the other hand, a strong Pd-Pd hopping is also observed. This is due to the spatial extension of the $4d$ orbitals, a consequence of its larger quantum number compared to $3d$ orbitals, that overlap with neighboring Pd ions; and the closer Pd-Pd distance in the octahedral environment. Since the hybridization matrix between the d -orbitals scales as d^{-4} , where d is the bond length, a shorter bond length greatly affects the hybridization between d -orbitals.⁵⁴ This will increase the kinetic energy, compared to the case of corner-shared and edge-shared octahedrons. Hence, the importance of correlations from direct Coulomb interactions will be highly dilute. Also, the lack of orbital degeneracy will eliminate the ferro-orbital correlation and the associated C-type antiferromagnetic order.⁵⁵

The strong covalency, absence of electronic correlations, lack of orbital degeneracy, and the dilute nature

of the magnetic frustration in PdTe are in sharp contrast, in particular, to Fe chalcogenides, and in general, to Fe-based superconductors. Thus, PdTe will display dramatically weaker magnetic and superconducting tendencies than the Fe-based superconductors. One may conclude that the key ingredients for a high T_c unconventional superconductivity are lost and pure PdTe may just be a low T_c superconductor. However, interesting magnetic correlation might be reactivated upon Fe doping.

IV. SUMMARY

We have performed self-consistent DFT and downfolding electronic band structure via symmetry respecting Wannier functions to study the electronic properties of PdTe. Our computations show that there is significant Pd- d and Te- p hybridization, larger crystal field splitting of Pd d -orbitals due to their near octahedral coordination, and higher filling of the Pd d -shell resulting in weaker magnetic frustration, strong covalency, and lack of orbital degeneracy, which quench ferro-orbital correlations. The large k_z variation of the Fermi surface topology also demonstrates a strong three-dimensional character of the electronic structure. These features destroy the ingredients needed for PdTe to be a high- T_c unconventional superconductor. This case study provides a good contrast that highlights some important features (quasi-two-dimensionality, proximity to half-filling, weaker covalency, and higher orbital degeneracy) of Fe-based high-temperature superconductors.

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